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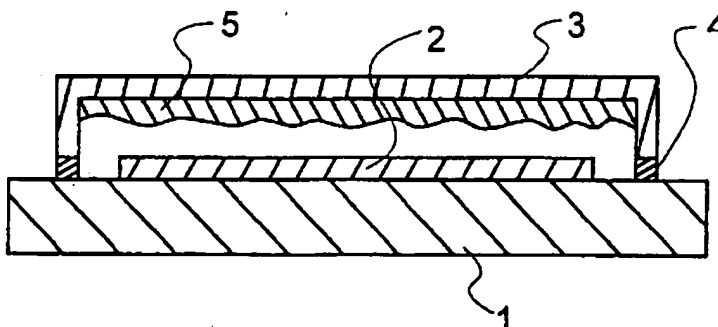
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(54) **Organic EL device**

(57) In an organic EL device comprising a substrate (1), an organic EL structure (2) on the substrate, and a sealing member (3) enclosing the organic EL structure, a mixture of a desiccant and an organic compound hav-

ing a melting point of 70-200°C is coated to the inside surface of the sealing member (3). The device maintains its initial performance over a long period of time and can be manufactured through simple sealing steps at low cost.

### FIG. 1



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## Description

[0001] This invention relates to an organic electroluminescent (EL) device using organic compounds, and more particularly, to a sealing means for protecting an organic EL structure on a substrate.

## BACKGROUND OF THE INVENTION

[0002] Recently, active research works have been made on organic EL devices. As a basic configuration, the organic EL device includes a hole injecting electrode, a thin film formed thereon by evaporating a hole transporting material such as triphenyldiamine (TPD), a light emitting layer deposited thereon of a fluorescent material such as an aluminum quinolinol complex (Alq3), and a metal electrode or electron injecting electrode formed thereon from a metal having a low work function such as magnesium. Such organic EL devices are attractive in that they can achieve a very high luminance ranging from several 100 to several 10,000 cd/m<sup>2</sup> with a drive voltage of approximately 10 volts.

[0003] Organic EL devices are very sensitive to moisture. Contact with moisture can cause serious problems including separation between the light emitting layer and the electrode layer, deterioration of constituent materials, formation of non-light-emitting zones known as dark spots, and reduction of the luminous area. As a result, the EL devices fail to maintain light emission of the desired quality.

[0004] One known solution to this problem is to shield an organic EL multilayer structure on a substrate from the exterior by tightly securing a gas-tight casing or sealing layer to the substrate so as to enclose the EL structure, as disclosed in JP-A 5-36475, 5-89959, and 7-169567.

[0005] Despite the provision of such casings or sealing layers, moisture gradually penetrates in the interior with the lapse of drive time whereby the devices deteriorate in several aspects, such as a drop of light emission luminance, generation or enlargement of dark spots, and reduction of the luminous area. Eventually the devices become unusable because of failure of light emission.

[0006] It was also proposed to accommodate the organic EL structure in a gas-tight casing in which a desiccant is contained. For example, JP-A 3-261091 discloses diphosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>) as the desiccant. However, P<sub>2</sub>O<sub>5</sub> tends to absorb moisture and becomes liquid (deliquescence) and thus forms phosphoric acid, which can be detrimental to the organic EL structure. The introduction of P<sub>2</sub>O<sub>5</sub> into the casing requires a careful limited procedure, which is impractical.

[0007] JP-A 6-176867 discloses an organic EL device enclosed with an external protective casing containing a fine powdery solid desiccant. Exemplary fine powdery solid desiccants are zeolite, active alumina, silica gel, and calcium oxide. The extra steps of introducing the

fine powdery solid desiccant into the casing and attaching the casing with the desiccant filled therein make the manufacturing process complex. If the desiccant of the type that physically adsorbs water, typically zeolite, is disposed within the casing in potential contact with the organic EL device, the desiccant releases the once adsorbed water by the heat associated with the light emission of the EL device. The lifetime of the device is not fully long.

[0008] JP-A 9-148066 discloses desiccants in the form of compounds capable of chemically adsorbing moisture and maintaining a solid state even after moisture absorption, for example, alkali metal oxides, alkaline earth metal oxides, sulfates, and metal halides. Because of the chemical adsorption, once water is adsorbed, these compounds no longer release the water, ensuring a longer lifetime to the device. However, the retention of the solid desiccant within the gas-tight case is difficult and requires extra steps, and the lifetime of the device is still insufficient.

[0009] JP-A 5-114486 and 5-41281 disclose to keep an organic EL device in an inert liquid compound in the form of a fluorocarbon containing a desiccant. This approach is effective to some extent for protecting the organic EL device from moisture, but requires the step of introducing the inert liquid compound containing a desiccant, that is, a cumbersome sealing step.

[0010] Of the prior art sealing techniques mentioned above, some are insufficient in suppressing degradation phenomena including a reduction of luminance with the lapse of driving time and the development and growth of dark spots. Other techniques have some sealing effects, but suffer from other problems including the complexity and expense of sealing steps.

## SUMMARY OF THE INVENTION

[0011] Therefore, an object of the invention is to provide an organic EL device which effectively suppresses the deterioration with time of the device including a reduction of luminance with the lapse of driving time and the development and growth of dark spots, maintains its initial performance over a long period of time, and can be manufactured through simple sealing steps at low cost.

[0012] The invention provides an organic electroluminescent (EL) device comprising a substrate, an organic EL structure formed on the substrate, and a sealing member enclosing the organic EL structure for providing a seal thereto. A mixture of a desiccant and an organic compound having a melting point of 70 to 200°C is disposed on the inside surface of the sealing member. The organic compound is preferably a wax-like compound, and especially a high molecular weight one.

## BRIEF DESCRIPTION OF THE DRAWING

[0013] The only figure, FIG. 1 is a schematic cross-

sectional view of an organic EL device according to one embodiment of the invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0014] The organic EL device of the invention has an organic EL structure formed on a substrate. A sealing member encloses the organic EL structure for sealing the structure from the exterior. A mixture of a desiccant and an organic compound having a melting point of 70 to 200°C is disposed on the inside of the sealing member. Since the mixture of a desiccant and a specific organic compound is disposed inside the sealing member that encloses the organic EL structure, the resulting construction is very simple and fully effective for sealing the organic EL structure. The manufacturing process is simple. Since moisture is effectively removed, the deterioration with time of the device is effectively restrained.

[0015] The organic compound used in admixture with the desiccant is not critical as long as it has a melting point (mp) of 70°C to 200°C, and especially 90°C to 150°C and remains in a solid state at the service temperature of the device. If the organic compound's melting point is below the above-defined range, a mixture of the desiccant and the organic compound can flow in a certain service environment. If the organic compound's melting point is above the above-defined range, it becomes difficult to dispose a mixture of the desiccant and the organic compound on the inside surface of the sealing member as by coating. Typically the organic compounds are waxes or high molecular weight organic compounds.

[0016] The wax used herein in combination with the desiccant is selected from those waxes that will not readily react with the desiccant. More particularly, an optimum wax for a particular desiccant may be selected from the following wax examples by considering its compatibility with the desiccant. Examples are naturally occurring waxes including petroleum waxes such as paraffin wax and microcrystalline wax, plant waxes, animal waxes, and mineral waxes. Also useful are organic compounds having equivalent characteristics to waxes such as fats and oils (e.g., so-called fats or solid fats). Effective components of waxes, fats and oils are hydrocarbons (e.g., alkane-series straight chain hydrocarbons having at least 22 carbon atoms), fatty acids (e.g., fatty acids of alkane-series straight chain hydrocarbons having at least 12 carbon atoms), fatty acid esters (e.g., saturated fatty acid esters resulting from saturated fatty acids having at least 20 carbon atoms and lower alcohols such as methyl alcohol), fatty acid amides (e.g., unsaturated fatty acid amides such as oleic amide and erucic amide), aliphatic amines (e.g., aliphatic primary amines having at least 16 carbon atoms), and higher alcohols (e.g., n-alkyl alcohols having at least 16 carbon atoms). Of these, petroleum waxes are especially preferred.

[0017] The high molecular weight compound or poly-

mer used herein in combination with the desiccant is preferably selected from those polymers which are easy to coat and will not readily react with the desiccant. More particularly, an optimum polymer for a particular desiccant may be selected from the following polymer examples by considering its compatibility with the desiccant. Examples are polyethylene (PE) resins and polypropylene (PP) resins as well as hot-melt polymers such as ethylene-vinyl acetate (EVA) copolymers having a vinyl acetate content of about 15 to 50%.

[0018] The desiccant used herein in combination with the organic compound is not critical as long as it is effective for absorbing moisture and will not readily react with the organic compound. Exemplary desiccants include calcium hydride ( $\text{CaH}_2$ ), strontium hydride ( $\text{SrH}_2$ ), barium hydride ( $\text{BaH}_2$ ), aluminum lithium hydride ( $\text{AlLiH}_4$ ), sodium oxide ( $\text{Na}_2\text{O}$ ), potassium oxide ( $\text{K}_2\text{O}$ ), calcium oxide ( $\text{CaO}$ ), barium oxide ( $\text{BaO}$ ), and magnesium oxide ( $\text{MgO}$ ). Of these desiccants, calcium hydride, strontium hydride, barium hydride, and aluminum lithium hydride are preferred.

[0019] On use, the desiccant is generally dispersed in the organic compound. The desiccant in particle form has a mean particle size of about 0.1 to 10  $\mu\text{m}$  though not limited thereto. An appropriate content of the desiccant is about 5 to 80% by weight, and especially about 20 to 70% by weight based on the mixture of desiccant and organic compound. A desiccant content of less than 5% by weight may fail to impart a sufficient moisture absorbing effect to the mixture. With a desiccant content of more than 80% by weight, it may become difficult to carry and support the desiccant by the organic compound, leaving the risk that the EL structure can be damaged by falling desiccant particles.

[0020] An appropriate amount of the mixture of the organic compound and the desiccant applied to the sealing member is 0.001 to 0.5  $\text{g}/\text{cm}^2$ , and especially 0.01 to 0.1  $\text{g}/\text{cm}^2$  although the amount varies with the specific gravity of the components used. Any application techniques including roll coating, blade coating, brush coating, and printing may be used while the use of a dispenser is also acceptable.

[0021] Referring to FIG. 1, there is illustrated one exemplary construction of the organic EL device according to the invention. On a substrate 1 is formed an organic EL structure 2. A sealing member 3 is placed on the substrate 1 so that the sealing member 3 encloses the organic EL structure 2 and is spaced therefrom. Specifically the sealing member 3 is secured to the substrate 1 with an adhesive 4 to define a sealed space between the sealing member 3 and the EL structure 2. A mixture 5 of a desiccant and an organic compound is disposed inside the sealing member 3, that is, on the inside surface of the sealing member 3 facing the EL structure 2. The mixture is preferably kept out of contact with the EL structure 2.

[0022] The sealing member is preferably in the form of a flat plate and is generally made of transparent or

translucent materials such as glass, quartz and resins, with glass being preferred. The use of a flat glass plate enables the low-cost manufacture of a thin organic EL display assembly. As the glass material, alkali glass is preferred from the economical aspect. Other preferred glass compositions are soda lime glass, lead alkali glass, borosilicate glass, aluminosilicate glass, and silica glass. Among others, surface-untreated plates of soda lime glass are preferred partially because of their low cost. Besides the plate glass, metal plates and plastic plates may be used as the sealing member.

[0023] The size of the sealing member is not particularly limited. The sealing member is appropriately sized in accordance with the design of a display area and the circuit design. Typically, the sealing member is about 0.1 to 5 mm thick when it is a flat plate. As in the illustrated embodiment, the sealing member may have a recess where the organic EL structure is partially or entirely received.

[0024] Means for adjusting the height of the sealing member above the substrate is preferably a spacer though not limited thereto. The use of a spacer enables low-cost easy adjustment to the desired height. The spacer may be made of resin beads, silica beads, glass beads, and glass fibers, with the glass beads being especially preferred. The spacer is generally comprised of particles having a narrow size distribution. The shape of spacer particles is not critical. Particles of various shapes may be used as long as they can serve as the spacer. The size of spacer particles is preferably about 1 to 20  $\mu\text{m}$ , more preferably about 1 to 10  $\mu\text{m}$ , and most preferably about 2 to 8  $\mu\text{m}$ , as expressed in equivalent circle diameter. Particles having a diameter within the range preferably have a length of less than about 100  $\mu\text{m}$ . The lower limit of length is not critical although it is at least equal to the diameter.

[0025] Where the sealing member is provided with a recess, the spacer may or may not be used. The spacer, if used, preferably has a size within the above-defined range, especially of 2 to 8  $\mu\text{m}$ .

[0026] The spacer may be premixed with a sealing adhesive or mixed with a sealing adhesive when applied. The content of the spacer in the sealing adhesive is preferably 0.01 to 30% by weight, and more preferably 0.1 to 5% by weight.

[0027] As the sealing adhesive used herein, adhesives of thermosetting type may be used, although adhesives of photo-curing type are preferred when their influence on the organic EL structure is considered. Examples include radical adhesives based on various acrylates (e.g., ester acrylates, urethane acrylates, epoxy acrylates, melamine acrylates, and acrylic resin acrylates) and urethane polyesters, cationic adhesives based on such resins as epoxy resins and vinyl ether resins, and thiol-ene addition type resin base adhesives. Of these, preferred are cationic adhesives which are free of oxygen hindrance and allow polymerization reaction to proceed even after light irradiation.

[0028] The cationic adhesive is preferably a UV curable epoxy resin-base adhesive of the cation curing type. The materials of the respective layers of the organic EL multilayer structure generally have a glass transition temperature of less than about 140°C, especially about 80 to 100°C. If conventional adhesives of the thermosetting type having a curing temperature of about 140 to 180°C are used, the organic EL structure softens upon curing of the adhesive, detracting from its characteristics. By contrast, UV curing type adhesives do not cause such softening of the organic EL structure. However, most UV curable adhesives commonly used at present are acrylic and thus have the problem that the acrylic monomer contained therein volatilizes upon curing and adversely affects the materials of the respective layers of the organic EL structure to deteriorate their characteristics. For this reason, a UV curable epoxy resin-base adhesive of the cation curing type which eliminates or substantially eliminates the above problem is used in the practice of the invention.

[0029] Among commercially available UV curable epoxy resin-base adhesives, epoxy resin-base adhesives of the combined UV/heat curing type are included. Most of these adhesives in which an acrylic resin of the radical curing type and an epoxy resin of the heat curing type are mixed or modified have not solved the problem of volatilization of acrylic monomer associated with the acrylic resins and the problem of curing temperature associated with the thermosetting epoxy resins. These adhesives are thus not suited for use with the organic EL device according to the invention.

[0030] The UV curable epoxy resin-base adhesive of the cation curing type is a composition comprising an epoxy resin as a base resin and a Lewis acid salt type curing agent capable of releasing a Lewis acid catalyst through photolysis upon exposure to light, typically ultraviolet radiation, as a main curing agent wherein the Lewis acid generated by light irradiation serves as a catalyst for the epoxy resin to polymerize through a cation polymerization type reaction mechanism until it is cured.

[0031] The epoxy resin as the base resin of the adhesive may be selected from among epoxidized olefin resins, alicyclic epoxy resins, and novolac epoxy resins. Examples of the curing agent include Lewis acid salts of aromatic diazonium, Lewis acid salts of diallyl iodonium, Lewis acid salts of triallyl sulfonium, and Lewis acid salts of triallyl selenium. Of these, Lewis acid salts of diallyl iodonium are preferred.

[0032] An appropriate amount of the adhesive applied is about  $6 \times 10^{-2}$  to  $2 \times 10^{-4}$  g/cm<sup>2</sup>, and especially about  $8 \times 10^{-3}$  to  $2 \times 10^{-4}$  g/cm<sup>2</sup> although the amount varies with the size of the organic EL structure and the type and organization of the display constructed by the organic EL device. The thickness of the adhesive layer should be sufficient to position the sealing member at a predetermined height above the substrate, that is, to provide a predetermined space above the organic EL structure on the substrate. In this sense, the thickness of the ad-

hesive layer is generally about  $5 \times 10^5$  to  $1 \times 10^3$  nm, preferably about  $5 \times 10^4$  to  $5 \times 10^3$  nm, and more preferably about  $2 \times 10^4$  to  $2 \times 10^3$  nm, though not limited thereto.

[0033] When the sealing member is attached to the EL structure-carrying substrate with the adhesive to seal the space, the space preferably contains a filler gas. The preferred filler gas is an inert gas such as argon (Ar), helium (He) or nitrogen ( $N_2$ ). The filler gas should preferably have a water content of up to about 100 ppm, more preferably up to about 10 ppm, and most preferably up to about 1 ppm. The lower limit of the water content is usually about 0.1 ppm though not critical.

[0034] As described above, transparent or translucent materials such as glass, quartz and resins are used as the substrate when light emitted by the EL structure exits from the substrate side. In the case of inversely stacked structure, the substrate may be either transparent or opaque, ceramics being useful as the opaque substrate.

[0035] The substrate may be provided with a color filter film, a fluorescent material-containing color conversion film or a dielectric reflecting film for controlling the color of light emission.

[0036] The color filter film used herein may be a color filter as used in liquid crystal displays and the like. The properties of a color filter may be adjusted in accordance with the light emission of the organic EL device so as to optimize the extraction efficiency and color purity. It is also preferred to use a color filter capable of cutting external light of short wavelength which is otherwise absorbed by the EL device materials and fluorescence conversion layer, because the light resistance and display contrast of the device are improved. An optical thin film such as a dielectric multilayer film may be used instead of the color filter.

[0037] The fluorescence conversion filter film is to convert the color of light emission by absorbing electroluminescence and allowing the fluorescent material in the film to emit light. It is formed from three components: a binder, a fluorescent material, and a light absorbing material. The fluorescent material used may basically have a high fluorescent quantum yield and desirably exhibits strong absorption in the electroluminescent wavelength region. In practice, laser dyes are appropriate. Use may be made of rhodamine compounds, perylene compounds, cyanine compounds, phthalocyanine compounds (including sub-phthalocyanines), naphthalimide compounds, fused ring hydrocarbon compounds, fused heterocyclic compounds, styryl compounds, and coumarin compounds. The binder is selected from materials which do not cause extinction of fluorescence, preferably those materials which can be finely patterned by photolithography or printing technique. Also, where the filter film is formed on the substrate so as to be contiguous to the hole injecting electrode, those materials which are not damaged during deposition of the hole injecting electrode (such as ITO or IZO) are preferable. The light absorbing material is used when the light ab-

sorption of the fluorescent material is short, and may be omitted if unnecessary. The light absorbing material may also be selected from materials which do not cause extinction of fluorescence of the fluorescent material.

[0038] Next, the organic EL structure constructing the organic EL device according to the invention is described. The organic EL structure includes on a substrate, a hole injecting electrode, an electron injecting electrode, and at least one organic layer disposed between the electrodes. The organic layer includes at least one hole transporting layer and at least one light emitting layer, on which the electron injecting electrode is disposed. A protective electrode may be disposed as the uppermost layer. The hole transporting layer may be omitted.

[0039] A transparent or translucent electrode is preferred as the hole injecting electrode because it is formed as an electrode on the substrate side and emitted light is to exit from the substrate side. Useful materials for transparent electrodes include tin-doped indium oxide (ITO), zinc-doped indium oxide (IZO), zinc oxide (ZnO), tin oxide ( $SnO_2$ ), and indium oxide ( $In_2O_3$ ), with ITO and IZO being preferred. Usually ITO contains  $In_2O_3$  and  $SnO_2$  in stoichiometry, while the oxygen content may deviate more or less therefrom.

[0040] The hole injecting electrode may have a sufficient thickness for hole injection and is preferably about 10 to about 500 nm thick, especially about 30 to 300 nm thick. Although no particular upper limit is imposed on the thickness of the electrode, too thick an electrode may have undesirable problems including separation, difficult processing, stress failure, lowering of light transmission, and leakage due to surface roughness. Inversely, too thin an electrode may have problems including film strength during preparation, hole transporting capability, and resistivity.

[0041] The hole injecting electrode layer can be formed by evaporation or other processes although sputtering is preferable.

[0042] The electrode on the light output side preferably has a transmittance of at least 50%, more preferably at least 60%, further preferably at least 80%, and especially at least 90% for each light emission in a luminous wavelength band, typically of 400 to 700 nm. The electrode with a low transmittance causes the light emission from the light emitting layer to attenuate, failing to provide a necessary luminance as the light emitting device. Where it is desired to increase the contrast for improving visibility, the electrode is given a relatively low transmittance.

[0043] The electron injecting electrode is preferably formed from materials having a low work function, for example, metal elements such as K, Li, Na, Mg, La, Ce, Ca, Sr, Ba, Al, Ag, In, Sn, Zn, and Zr, and binary or ternary alloys made of two or three such metal elements for stability improvement. Exemplary alloys are Ag-Mg (Ag: 1 to 20 at%), Al-Li (Li: 0.3 to 14 at%), In-Mg (Mg: 50 to 80 at%), and Al-Ca (Ca: 5 to 20 at%). Oxides of

these metals may also be formed in combination with an auxiliary electrode. It is understood that the electron injecting electrode can also be formed by evaporation or sputtering.

[0044] The electron injecting electrode thin film may have a sufficient thickness for electron injection, for example, a thickness of at least 0.1 nm, preferably at least 1 nm. Although the upper limit is not critical, the electrode thickness is typically about 1 to about 500 nm. On the electron injecting electrode, a protective electrode may be provided, if desired.

[0045] The protective electrode has a thickness sufficient to ensure efficient electron injection and prevent ingress of moisture, oxygen and organic solvents, preferably a thickness of at least 50 nm, more preferably at least 100 nm, and especially 100 to 1,000 nm. Too thin a protective electrode layer would fail to achieve the above effects or to provide step coverage so that its connection to a terminal electrode becomes insufficient. Too thick a protective electrode layer would accumulate more stresses, resulting in an increased growth rate of dark spots.

[0046] The total thickness of the electron injecting electrode and the protective electrode combined is preferably about 100 to 1,000 nm though not critical.

[0047] Following the electrode formation, a protective film may be formed in addition to the protective electrode, using an inorganic material such as SiO<sub>x</sub> or an organic material such as Teflon and chlorine-containing fluorinated hydrocarbon polymers. The protective film may be either transparent or opaque and have a thickness of about 50 to 1,200 nm. Apart from the reactive sputtering process, the protective film may also be formed by an ordinary sputtering, evaporation or PECVD process.

[0048] Next, the organic material layers included in the organic EL structure are described.

[0049] The light emitting layer is a laminated film comprising an organic compound thin film of at least one type participating in at least a light emitting function.

[0050] The light emitting layer has the functions of injecting holes and electrons, transporting them, and recombining holes and electrons to create excitons. The use of relatively electronically neutral compounds in the light emitting layer enables effective and well-balanced injection and transportation of electrons and holes.

[0051] If desired, the light emitting layer includes a hole injecting and transporting layer and an electron injecting and transporting layer both of organic compounds as well as the light emitting layer in a narrower sense.

[0052] The hole injecting and transporting layer has the functions of facilitating injection of holes from the hole injecting electrode, transporting holes stably, and blocking electrons. The electron injecting and transporting layer has the functions of facilitating injection of electrons from the electron injecting electrode, transporting electrons stably, and blocking holes. These layers are

effective for increasing the number of holes and electrons injected into the light emitting layer and confining holes and electrons therein for optimizing the recombination region to improve light emission efficiency.

[0053] The thicknesses of the light emitting layer, the hole injecting and transporting layer, and the electron injecting and transporting layer are not critical and vary with a particular formation technique. Usually, their thickness is preferred to range from about 5 nm to about 500 nm, especially about 10 nm to about 300 nm.

[0054] The thickness of the hole injecting and transporting layer and the electron injecting and transporting layer is equal to or ranges from about 1/10 times to about 10 times the thickness of the light emitting layer although it depends on the design of a recombination/light emitting region. When the electron or hole injecting and transporting layer is divided into an injecting layer and a transporting layer, preferably the injecting layer is at least 1 nm thick and the transporting layer is at least 1 nm thick. The upper limit of thickness is usually about 500 nm for the injecting layer and about 500 nm for the transporting layer. The same film thickness applies when two injecting/transporting layers are provided.

[0055] The light emitting layer of the organic EL device contains a fluorescent material that is a compound having a light emitting capability. The fluorescent material may be at least one member selected from compounds as disclosed, for example, in JP-A 63-264692, such as quinacridone, rubrene, and styryl dyes. Also, quinoline derivatives such as metal complex dyes having 8-quinolinol or a derivative thereof as the ligand such as tris(8-quinolinolato)aluminum are included as well as tetraphenylbutadiene, anthracene, perylene, coronene, and 12-phthaloperinone derivatives. Further useful are the phenylanthracene derivatives described in JP-A 8-12600 and the tetraarylethene derivatives described in JP-A 8-12969.

[0056] It is preferred to use such a compound in combination with a host material capable of light emission by itself, that is, to use the compound as a dopant. In this embodiment, the content of the compound in the light emitting layer is preferably 0.01 to 10% by weight, especially 0.1 to 5% by weight. By using the compound in combination with the host material, the light emission wavelength of the host material can be altered, allowing light emission to be shifted to a longer wavelength and improving the luminous efficacy and stability of the device.

[0057] As the host material, quinolinolato complexes are preferable, with aluminum complexes having 8-quinolinol or a derivative thereof as the ligand being more preferable. These aluminum complexes are disclosed in JP-A 63-264692, 3-255190, 5-70773, 5-258659 and 6-215874.

[0058] Illustrative examples include tris(8-quinolinolato)aluminum, bis(8-quinolinolato)magnesium, bis(benzo(f)-8-quinolinolato)zinc, bis(2-methyl-8-quinolinolato)aluminum oxide, tris(8-quinolinolato)indium, tris

(5-methyl-8-quinolinolato)aluminum, 8-quinolinolato-lithium, tris(5-chloro-8-quinolinolato)gallium, bis(5-chloro-8-quinolinolato)calcium, 5,7-dichloro-8-quinolinolatoaluminum, tris(5,7-dibromo-8-hydroxyquinolinolato)aluminum, and poly[zinc(II)-bis(8-hydroxy-5-quinolinyl)methane].

[0059] Also useful are aluminum complexes having another ligand in addition to 8-quinolinol or a derivative thereof. Examples include bis(2-methyl-8-quinolinolato)(phenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(orthocresolato)aluminum(III), bis(2-methyl-8-quinolinolato)(meta-cresolato)aluminum(III), bis(2-methyl-8-quinolinolato)(para-cresolato)aluminum(III), bis(2-methyl-8-quinolinolato)(ortho-phenylphenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(meta-phenylphenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(para-phenylphenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(2,3-dimethylphenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(2,6-dimethylphenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(3,4-dimethylphenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(3,5-dimethylphenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(3,5-di-tert-butylphenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(2,6-diphenylphenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(2,4,6-triphenylphenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(2,3,6-trimethylphenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(2,3,5,6-tetramethylphenolato)aluminum(III), bis(2-methyl-8-quinolinolato)(1-naphtholato)aluminum(III), bis(2-methyl-8-quinolinolato)(2-naphtholato)aluminum(III), bis(2,4-dimethyl-8-quinolinolato)(ortho-phenylphenolato)aluminum(III), bis(2,4-dimethyl-8-quinolinolato)(para-phenylphenolato)aluminum(III), bis(2,4-dimethyl-8-quinolinolato)(metaphenylphenolato)aluminum(III), bis(2,4-dimethyl-8-quinolinolato)(3,5-dimethylphenolato)aluminum(III), bis(2,4-dimethyl-8-quinolinolato)(3,5-di-tert-butylphenolato)aluminum(III), bis(2-methyl-4-ethyl-8-quinolinolato)(para-cresolato)aluminum(III), bis(2-methyl-4-methoxy-8-quinolinolato)(para-phenylphenolato)aluminum(III), bis(2-methyl-5-cyano-8-quinolinolato)(orthocresolato)aluminum(III), and bis(2-methyl-6-trifluoromethyl-8-quinolinolato)(2-naphtholato)aluminum(III).

[0060] Also acceptable are bis(2-methyl-8-quinolinolato)aluminum(III)-u-oxo-bis(2-methyl-8-quinolinolato)aluminum(III), bis(2,4-dimethyl-8-quinolinolato)aluminum(III)-u-oxo-bis(2,4-dimethyl-8-quinolinolato)aluminum(III), bis(4-ethyl-2-methyl-8-quinolinolato)aluminum(III), bis(2-methyl-4-methoxyquinolinolato)aluminum(III)-u-oxo-bis(2-methyl-4-methoxyquinolinolato)aluminum(III), bis(5-cyano-2-methyl-8-quinolinolato)aluminum(III)-u-oxo-bis(5-cyano-2-methyl-8-quinolinolato)aluminum(III), and bis(2-methyl-5-trifluoromethyl-8-quinolinolato)aluminum(III)-u-oxo-bis(2-methyl-5-trifluoromethyl-8-quinolinolato)aluminum(III).

[0061] Other useful host materials are the phenylanthracene derivatives described in JP-A 8-12600 and the

tetraarylethene derivatives described in JP-A 8-12969.

[0062] The light emitting layer may also serve as the electron injecting and transporting layer. In this case, tris(8-quinolinolato)aluminum etc. are preferably used.

These fluorescent materials may be evaporated.

[0063] Also, if necessary, the light emitting layer may be a layer of a mixture of at least one hole injecting and transporting compound and at least one electron injecting and transporting compound, in which a dopant is preferably contained. In such a mix layer, the content of the dopant is preferably 0.01 to 20% by weight, especially 0.1 to 15% by weight.

[0064] In the mix layer, carrier hopping conduction paths are created, allowing carriers to move through a polarly predominant material while injection of carriers of opposite polarity is rather inhibited, and the organic compound becomes less susceptible to damage, resulting in the advantage of an extended device life. By incorporating the aforementioned dopant in such a mix layer, the light emission wavelength the mix layer itself possesses can be altered, allowing light emission to be shifted to a longer wavelength and improving the luminous intensity and stability of the device.

[0065] The hole injecting and transporting compound and electron injecting and transporting compound used in the mix layer may be selected from compounds for the hole injecting and transporting layer and compounds for the electron injecting and transporting layer to be described later, respectively. Inter alia, the compound for the hole injecting and transporting layer is preferably selected from amine derivatives having strong fluorescence, for example, triphenyldiamine derivatives which are hole transporting materials, styrylamine derivatives and amine derivatives having an aromatic fused ring.

[0066] The electron injecting and transporting compound is preferably selected from quinoline derivatives and metal complexes having 8-quinolinol or a derivative thereof as a ligand, especially tris(8-quinolinolato)aluminum (Alq3). The aforementioned phenylanthracene derivatives and tetraarylethene derivatives are also preferable.

[0067] For the hole injecting and transporting layer, amine derivatives having intense fluorescence are useful, for example, the triphenyldiamine derivatives, styrylamine derivatives, and amine derivatives having an aromatic fused ring, exemplified above as the hole transporting material.

[0068] The mix ratio is preferably determined in accordance with the carrier density and carrier mobility. It is usually preferred that the weight ratio of the hole injecting and transporting compound to the electron injecting and transporting compound range from about 1/99 to about 99/1, more preferably from about 10/90 to about 90/10, especially from about 20/80 to about 80/20.

[0069] Also preferably, the thickness of the mix layer ranges from the thickness of a mono-molecular layer to less than the thickness of the organic compound layer, specifically from 1 to 85 nm, more preferably 5 to 60 nm,

especially 5 to 50 nm.

[0070] Preferably the mix layer is formed by a co-deposition process of evaporating the compounds from distinct sources. If both the compounds have approximately equal or very close vapor pressures or evaporation temperatures, they may be pre-mixed in a common evaporation boat, from which they are evaporated together. The mix layer is preferably a uniform mixture of both the compounds although the compounds can be present in island form. The light emitting layer is generally formed to a predetermined thickness by evaporating an organic fluorescent material or coating a dispersion thereof in a resin binder.

[0071] In the hole injecting and transporting layer, there may be used various organic compounds as described, for example, in JP-A 63-295695, 2-191694, 3-792, 5-234681, 5-239455, 5-299174, 7-126225, 7-126226, and 8-100172, and EP 0650955A1. Exemplary are tetraarylbenzidine compounds (triaryldiamines or triphenyldiamines: TPD), aromatic tertiary amines, hydrazone derivatives, carbazole derivatives, triazole derivatives, imidazole derivatives, oxadiazole derivatives having an amino group, and polythiophenes. Two or more of these compounds may be used, and on such combined use, they may be formed as separate layers or mixed.

[0072] In the electron injecting and transporting layer, there may be used quinoline derivatives including organic metal complexes having 8-quinolinol or a derivative thereof as a ligand such as tris(8-quinolinolato)aluminum (Alq3), oxadiazole derivatives, perylene derivatives, pyridine derivatives, pyrimidine derivatives, quinoxaline derivatives, diphenylquinone derivatives, and nitro-substituted fluorene derivatives. The electron injecting and transporting layer can also serve as the light emitting layer. In this case, use of tris(8-quinolinolato)aluminum etc. is preferred. Like the light emitting layer, the electron injecting and transporting layer may be formed by evaporation or the like.

[0073] Where the electron injecting and transporting layer is formed separately as an electron injecting layer and an electron transporting layer, two or more compounds are selected in a proper combination from the compounds commonly used in electron injecting and transporting layers. In this regard, it is preferred to stack layers in such an order that a layer of a compound having a greater electron affinity may be disposed adjacent the electron injecting electrode. The order of stacking also applies where a plurality of electron injecting and transporting layers are provided.

[0074] In forming the hole injecting and transporting layer, the light emitting layer, and the electron injecting and transporting layer, vacuum evaporation is preferably used because homogeneous thin films are available. By utilizing vacuum evaporation, there is obtained a homogeneous thin film which is amorphous or has a crystal grain size of less than 0.2  $\mu\text{m}$ . If the grain size is more than 0.2  $\mu\text{m}$ , uneven light emission would take place and

the drive voltage of the device must be increased with a substantial drop of hole injection efficiency.

[0075] The conditions for vacuum evaporation are not critical although a vacuum of  $10^{-4}$  Pa or lower and a deposition rate of about 0.01 to 1 nm/sec are preferred. It is preferred to successively form layers in vacuum because the successive formation in vacuum can avoid adsorption of impurities on the interface between the layers, thus ensuring better performance. Also, the drive voltage of a device can be reduced and the development and growth of dark spots be restrained.

[0076] In the embodiment wherein the respective layers are formed by vacuum evaporation, where it is desired for a single layer to contain two or more compounds, boats having the compounds received therein are individually temperature controlled to achieve co-deposition.

[0077] The organic EL device of the invention is generally of the dc or pulse drive type while it can be of the ac drive type. The applied voltage is generally about 2 to 30 volts.

#### EXAMPLE

[0078] Examples of the present invention are given below by way of illustration and not by way of limitation.

##### Preparation of desiccant/resin mixture sample 1

[0079] Wax (mp. about 90°C) available under the trade name of Proof Wax from Nikka Seiko K.K. was used as the organic compound, and calcium hydride ( $\text{CaH}_2$ ) used as the desiccant. The wax was heated up to 150°C in a nitrogen atmosphere having a moisture content of up to 100 ppm. To 100 parts by weight of the wax was added 100 parts by weight of the desiccant. They were mixed and agitated, obtaining a desiccant/resin mixture. The mixture was heated and melted at 170°C and applied to the inside surface of a sealing glass plate (which was to face an organic EL structure when assembled). The amount of the mixture coated was about 0.05 g/cm<sup>2</sup>.

[0080] The thus coated glass plate was allowed to stand at room temperature for cooling. At room temperature, the desiccant/resin mixture solidified and gave rise to no flow phenomenon. It was confirmed that the desiccant was secured to the sealing glass plate by a very easy process.

##### Preparation of desiccant/resin mixture sample 2

[0081] A polyethylene resin (mp. 118°C) available under the trade name of Hiwax 410P from Mitsui Chemical K.K. was used as the organic compound, and calcium hydride ( $\text{CaH}_2$ ) used as the desiccant. The resin was heated up to 150°C in a nitrogen atmosphere having a moisture content of up to 100 ppm. To 100 parts by weight of the resin was added 100 parts by weight of the



desiccant. They were mixed and agitated, obtaining a desiccant/resin mixture. The mixture was heated and melted at 170°C and applied to the inside surface of a sealing glass plate (which was to face an organic EL structure when assembled). The amount of the mixture coated was about 0.05 g/cm<sup>2</sup>.

[0082] The thus coated glass plate was allowed to stand at room temperature for cooling. At room temperature, the desiccant/resin mixture solidified and gave rise to no flow phenomenon. It was confirmed that the desiccant was secured to the sealing glass plate by a very easy process.

#### Preparation of organic EL device

[0083] A 7059 glass substrate (Corning Glass Works) was scrubbed using a neutral detergent. By effecting RF magnetron sputtering of an indium tin oxide target while setting the glass substrate at 250°C, an ITO hole injecting electrode layer was formed on the glass substrate to a thickness of 200 nm. The substrate having the ITO electrode layer formed thereon was surface cleaned with UV/ozone.

[0084] The substrate was then secured by a holder in a vacuum evaporation chamber, which was evacuated to a vacuum of  $1 \times 10^{-4}$  Pa or lower. 4,4',4''-tris(N-(3-methylphenyl)-N-phenylamino)triphenylamine (m-MTDATA) was evaporated at a deposition rate of 0.1 nm/sec. to a thickness of 55 nm, forming a hole injecting layer. Then, N,N'-diphenyl-N,N'-m-tolyl-4,4'-diamino-1,1'-biphenyl (TPD) was evaporated at a deposition rate of 0.1 nm/sec to a thickness of 20 nm, forming a hole transporting layer.

[0085] With the vacuum kept, N,N,N',N'-tetrakis(m-biphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), tris(8-quinolinolato)aluminum (Alq3), and rubrene were evaporated at an overall deposition rate of 0.2 nm/sec to a thickness of 100 nm, forming a light emitting layer. The light emitting layer was a mixture of TPD and Alq3 in a weight ratio of 1:1, doped with 10% by volume of rubrene.

[0086] With the vacuum kept, AILi (Li, 7 at%) was evaporated to a thickness of 1 nm, and aluminum was successively evaporated to a thickness of 200 nm, forming an electron injecting electrode and an auxiliary electrode, respectively.

[0087] The sealing glass plate having the desiccant/organic compound mixture (Sample 1 or 2) coated on the inside surface was laid on the substrate so as to enclose the EL structure inside and secured thereto with an epoxy resin adhesive of the photo-curing type, completing an EL assembly (designated Assembly Sample 1 or 2). For comparison purposes, a sealing glass plate without the desiccant/organic compound mixture coating was similarly secured to the substrate, forming a comparative EL assembly.

[0088] In an environment of 60°C and RH 95%, ten samples for each of the EL assemblies were continuously driven at a current density of 10 mA/cm<sup>2</sup>. After 500

hours of continuous driving, the light emitting surface was visually observed to count dark spots per pixel. In Assembly Samples 1 and 2 within the scope of the invention, only about two dark spots having a diameter of less than 50  $\mu$ m were found. In the Comparative Sample, more than 15 dark spots having a diameter of more than 50  $\mu$ m were found.

[0089] There has been described an organic EL device which effectively suppresses the deterioration with time of the device including a reduction of luminance with the lapse of driving time and the development and growth of dark spots, maintains its initial performance over a long period of time, and can be manufactured through simple sealing steps at low cost.

[0090] Japanese Patent Application No. 10-370280 is incorporated herein by reference.

[0091] The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

#### Claims

1. An organic electroluminescent device comprising a substrate, an organic electroluminescent structure formed on the substrate, and a sealing member enclosing the organic electroluminescent structure for providing a seal thereto,  
a mixture of a desiccant and an organic compound having a melting point of 70 to 200°C being disposed on the inside surface of said sealing member.
2. The device of claim 1 wherein said organic compound is a wax-like compound.
3. The device of claim 1 wherein said organic compound is a high molecular weight one.

FIG. 1

